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AERONUTRONIC

A DIVISION OF

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RESEARCH LABORATORIES

TECHNICAL REPORT

AN EXPERIMENTAL PROGRAM FOR OBTAINING THE
THERMODYNAMIC PROPERTIES OF PROPELLANT
COMBUSTION PRODUCTS

THIRD QUARTERLY TECHNICAL SUMMARY REPORT

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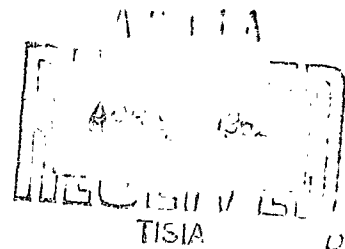
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15 March 1962

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FORD ROAD / NEWPORT BEACH, CALIFORNIA



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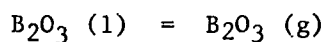
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SUMMARY

Torsion vapor pressure studies on lithium oxide and boric oxide have been completed. A final and self-consistent set of results has been obtained using platinum effusion cells equipped with internal black-body cavities. For Li_2O , pressures measured over the range 1480 to 1670°K are higher than calculated elemental decomposition pressures by a factor of about 2.7, indicating vaporization to a stable gaseous oxide molecule. The results are consistent with a heat of sublimation at 298°K of 100 kcal/mole for Li_2O (g) and a heat of formation at 298°K of -42 kcal/mole. Reliable molecular constant data are needed for Li_2O before definitive thermal data can be derived.

The vapor pressure of B_2O_3 has been measured in the range 1400 to 1570°K. A vibrational frequency assignment for B_2O_3 (g) based on matrix isolation spectra yields for the reaction



an average third-law ΔH_{298} of 98.7 kcal/mole and a second-law value of 99.4 kcal/mole. A corresponding analysis using thermal functions based on vapor emission spectral data leads to second- and third-law ΔH_{298} values of 101.2 and 91.7 kcal/mole, respectively. If the matrix isolation data are accepted as the more reliable, the heat of formation of B_2O_3 (g)

at 298°K is derived as -202.0 kcal/mole.

The vaporization of beryllium fluoride has been studied by the torsion-effusion method in the range 810 to 945°K. Second- and third-law methods have been used to derive the heat of sublimation of BeF₂ at 298°K as 58.0 kcal/mole, leading to $\Delta H_{298}^{\circ} = -183.2$ kcal/mole for BeF₂ (g). From studies of the vaporization of Be-BeF₂ mixtures, a lower limit of -60 kcal/mole has been derived for the heat of formation of BeF (g) at 298°K.

Temperature dependences of shutter-check intensities of BOF⁺ and (BOF)₃⁺ ions from equilibrium vapors over MgF₂ - B₂O₃ mixtures in the mass spectrometer lead to the value -144 ± 3 kcal/mole for the heat of formation of BOF (g) at 298°K. The effect of shutter position on ion intensity is discussed for vapor species which are partially noncondensable. Evidence for the absence of a large fragmentation contribution to BOF⁺ intensities for 17-volt ionizing electrons is presented.

Specific-heat data obtained on tantalum by the vacuum cooling rate method in the range 1200 to 1700°K are in reasonable agreement with accepted values, indicating that the method is workable.

A summary of current "best values" of thermal properties obtained from this program has been prepared and is included in this report.

SECTION 1

INTRODUCTION

The studies reported here are part of an experimental program designed to provide thermodynamic data required in the analysis of propulsion systems. Specific areas of study are the thermodynamics of vaporization of light metal compounds and the specific heats of condensed phases. Vaporization data, from which heats and free energies of formation of important species can be derived, are being obtained by effusion, transpiration, and mass spectrometric techniques. A method is under development for determination of specific heats from measurement of vacuum cooling rates.

The results of some of these studies are described in the following sections.

SECTION 2

EFFUSION STUDIES

2.1 EXPERIMENTAL

Torsion cells fabricated from platinum have been used in vaporization studies on the metal oxide systems reported below. Since the platinum cells differ in some respects from the graphite cells used in previous studies, a brief description is in order. The platinum cells were formed from 0.023-cm-thick sheet into cubical boxes 2.0 cm on a side. All seams were made vacuum-tight by gas-oxygen welding. An internal black-body cavity for pyrometer temperature measurement was provided by a platinum thimble 1.5 cm long and 0.7 cm in diameter with its open end welded to the bottom of the cell. The thimble was totally enclosed within the cell. Temperatures could be measured with an optical pyrometer by sighting into a 0.15-cm-diameter orifice in a plate covering the open end of the thimble. The hemispherical cap on the thimble and the small sight hole should insure multiple reflection of the emitted radiation and, therefore, close approach to black-body behavior. Each cell contained four effusion orifices, one in each of the four vertical faces, with moment arms of about 0.8 cm. The cell was suspended from a 0.125-cm-diameter platinum rod. All other features of the torsion system are the same as described in previous reports.

2.2 THE VAPORIZATION OF BORIC OXIDE

Some preliminary data on the vapor pressure of boric oxide were given in a previous report.¹ Because of uncertainties in temperature measurement and defects in effusion cell design, the measurements have been repeated using the platinum effusion cells described in Section 2.1. These latter cells gave entirely satisfactory results. The data are needed in analyzing the vaporization behavior of metal borate systems and should also be helpful in deciding on a firm vibrational assignment for B_2O_3 (g).

Vapor pressure measurements were made by the torsion-effusion method on an Amend Drug Company sample of CP B_2O_3 which was vacuum dried for several hours at 1200°C . Details of the torsion-effusion method have been given in previous reports. Vapor pressure data obtained with two effusion cells of different orifice size are summarized in Table I. Pressures were computed from the relation

$$P_T = \frac{2k\theta}{\Sigma afq} \quad (1)$$

where k is the torsion constant of the filament, θ is the observed angular deflection, and a , f , and q are the area, force factor, and moment arm of each of the effusion orifices. In Figure 1 the results are shown graphically. There is no observable dependence of pressure on orifice size, indicating a condensation coefficient close to unity. The data reported here are in reasonably good agreement with the recent results of White, Walsh, Goldstein, and Dever² but differ somewhat in temperature dependence from the results of Nesmeyanov and Firsova.³ Although the second-law heat of 91.0 ± 1 kcal/mole at 1500°K is higher than most values obtained previously by effusion weight-loss studies, the present results are less likely to be in error at the lower temperatures where water impurity causes appreciable evolution of HBO_2 (g) and spuriously high pressures. In the torsion-effusion work the sample is maintained under high vacuum throughout the course of the measurements; any initial water impurity is removed after several heating cycles.

TABLE I
THE VAPOR PRESSURE OF BORIC OXIDE

Pt Cell 7		Pt Cell 8	
T°K	P _T x 10 ⁵ , atm	T°K	P _T x 10 ⁵ , atm
Series I		Series I	
1454	0.73	1544	5.01
1475	1.16	1534	4.11
1493	1.67	1520	3.21
1514	2.66	1509	2.73
1567	7.31	1494	2.04
1557	6.25	1483	1.43
1547	5.40	1469	1.11
1530	3.63	1441	0.52
1521	3.20	1405	0.24
1505	2.57		
1451	0.82		
Series II		Series II	
1422	0.39	1543	5.14
1527	3.83	1532	4.23
1562	7.16	1509	2.65
1510	2.65	1496	2.04
		1486	1.66
		1462	0.99
		1437	0.50

$$\bar{a} = 0.0051 \text{ cm}^2$$

$$\Sigma afq = 0.01318 \text{ cm}^3$$

$$k = 3.06 \text{ dyne cm/rad}$$

$$\bar{a} = 0.0107 \text{ cm}^2$$

$$\Sigma afq = 0.02849 \text{ cm}^3$$

$$k = 3.05 \text{ dyne cm/rad}$$

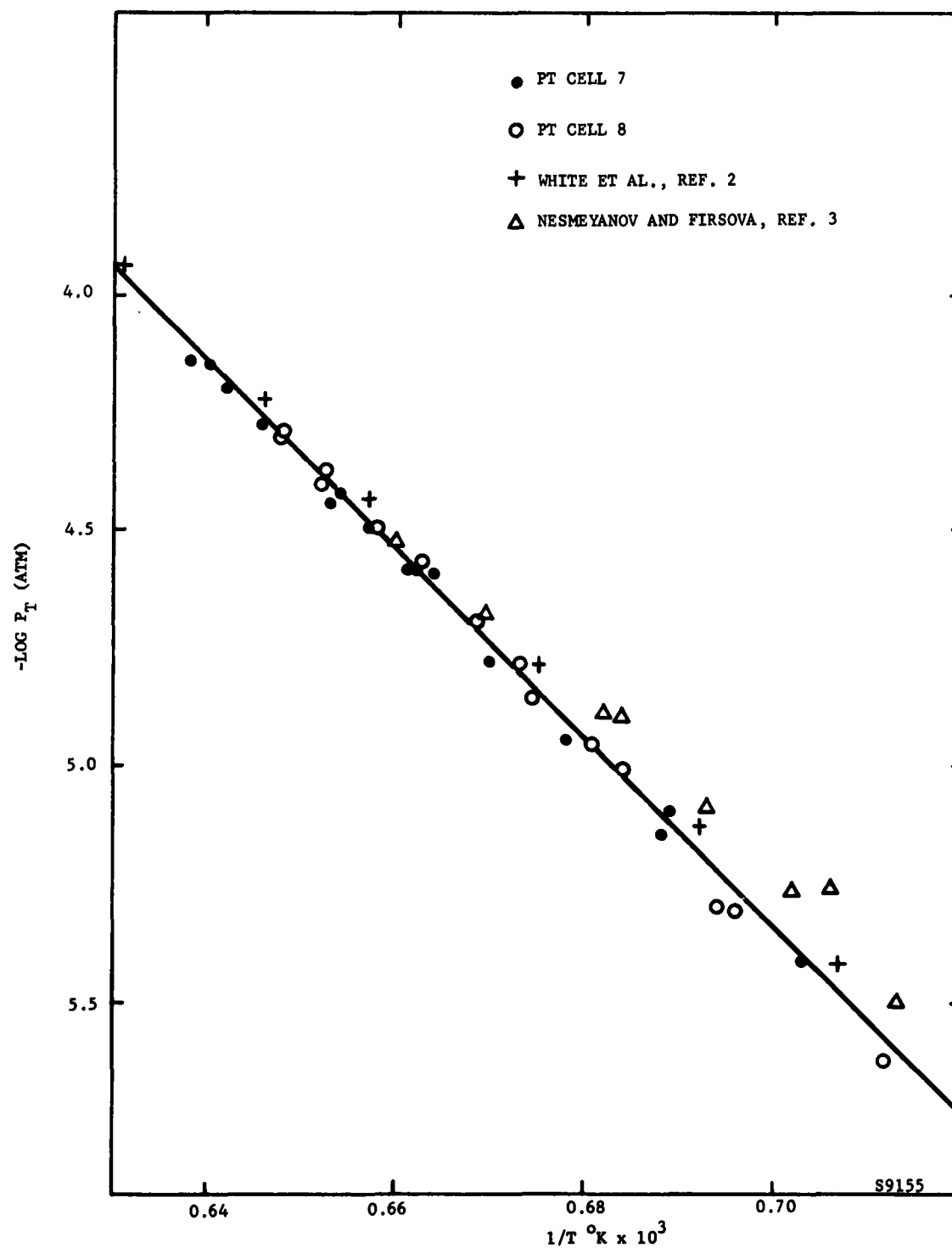


FIGURE 1. THE VAPOR PRESSURE OF BORIC OXIDE

The thermodynamic functions of B_2O_3 (g) are not firmly established because of uncertainties in the vibrational frequency assignment. However, the torsion vapor pressure data can be examined for compatibility with two recent tentative assignments, one based on vapor emission spectra⁴ and one based on matrix isolation spectra.⁵ A comparison of second- and third-law heats of vaporization of B_2O_3 , calculated from thermodynamic functions derived from the data of references (4) and (5), is given in Table II. B_2O_3 vapor is known to be monomeric. The agreement between second and third-law heats and the constancy of the third-law values would indicate that the vapor pressure data reported here favor the frequency assignment based on the matrix isolation spectra. In terms of entropy, the data of references 4 and 5 yield calculated entropies of 94.7 and 100.6 cal/mole deg, respectively, for B_2O_3 (g) at 1500°K; from the second-law heat, the measured vapor pressure, and the entropy of liquid B_2O_3 ⁶, one derives an experimental entropy of 101.1 cal/mole deg at 1500°K.

Until a firm vibrational assignment is adopted, the thermal properties of B_2O_3 (g) must be considered uncertain. If the assignment of reference 5 is accepted as being more nearly correct, the heat of formation of B_2O_3 (g) at 298°K is derived as -202.0 kcal/mole. The vapor pressure data reported here, however, are felt to be definitive and thus supersede the preliminary data given earlier.¹

TABLE II

COMPARISON OF DERIVED HEATS FOR



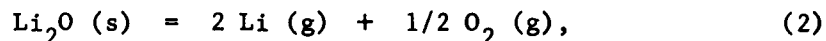
T°K	$\frac{\Delta F}{T}$	Vapor Emission Data ⁴		Matrix Isolation Data ⁵	
		$\Delta \left(\frac{F-H_{298}}{T} \right)^*$	ΔH_{298}	$\Delta \left(\frac{F-H_{298}}{T} \right)^*$	ΔH_{298}
	cal/mole deg	cal/mole deg	kcal/mole	cal/mole deg	kcal/mole
1400	25.7	40.1	92.1	44.9	98.8
1450	23.4	39.9	91.8	44.7	98.7
1500	21.3	39.7	91.5	44.5	98.7
1550	19.4	39.5	91.3	44.3	98.7
		ΔH_{298} (2nd law) =		ΔH_{298} (2nd law) =	
		101.2 \pm 1 kcal/mole		99.4 \pm 1 kcal/mole	

* Free-energy functions for $\text{B}_2\text{O}_3 (\ell)$ taken from reference 6.

2.3 THE VAPORIZATION OF LITHIUM OXIDE

Preliminary vaporization data were also given for lithium oxide in a previous report.⁷ Additional vapor pressure studies have been carried out with the platinum effusion cells described above and a final and self-consistent set of results has been obtained. Vapor pressures were measured by the torsion method on samples of crystalline Li_2O prepared by thermal decomposition of reagent-grade lithium carbonate. The Li_2CO_3 was decomposed under high vacuum by gradually raising the temperature to 1200°C and pumping off the CO_2 . After the initial loading of the effusion cell, the Li_2O sample was kept under high vacuum until the completion of the measurements. Repeated contamination by atmospheric CO_2 and water vapor was thus avoided.

The final vapor pressure data are summarized in Table III and are shown graphically in Figure 2. The measured pressures show no dependence on orifice size and must, therefore, be equilibrium values. An apparent hole-size effect reported earlier⁷ may have been due to incomplete outgassing; steady and reproducible pressures were obtained only after prolonged outgassing at the highest temperatures. The torsion pressures are somewhat lower than the Knudsen effusion data of Brewer and Margrave⁸ and Nesmeyanov and Belykh⁹, possibly because of repeated contamination of the samples with atmospheric gases in the course of the Knudsen effusion studies. However, the pressures reported here are 2.5 to 3 times higher than pressures calculated for the decomposition process



indicating vaporization primarily to a stable gaseous oxide molecule. This result differs from that reported by Berkowitz, et al.¹⁰, in which mass spectrometric studies of Li_2O vaporization were interpreted as indicating less than 10 percent of gaseous oxide species in the saturated

TABLE III

THE VAPOR PRESSURE OF LITHIUM OXIDE

<u>Pt Cell 7</u>		<u>Pt Cell 8</u>	
T°K	$P_T \times 10^5, \text{ atm}$	T°K	$P_T \times 10^5, \text{ atm}$
Series I		Series I	
1627	5.24	1564	2.26
1610	3.90	1575	2.42
1598	3.26	1597	3.44
1572	2.13	1596	3.30
1558	1.83	1575	2.22
1530	1.18	1569	2.20
1512	0.83	1553	1.59
1498	0.70	1514	0.73
		1589	2.88
		1575	2.28
		1538	1.15
		1525	0.94
		1494	0.54
Series II		Series II	
1635	5.57		
1602	3.52		
1587	2.73		
1575	2.35		
1549	1.57		
1512	0.87		
1655	7.96	1626	4.80
1628	5.48	1615	4.59
		1605	3.98
		1587	2.65
		1565	1.94
Series III		Series III	
1606	3.48		
1562	1.80		
1638	5.98	1609	4.05
1616	4.43	1592	3.63
1590	2.94	1588	2.87
1563	1.93	1616	4.62
1523	0.93	1562	1.63
		1557	1.60
$\bar{a} = 0.0051 \text{ cm}^2$		$\bar{a} = 0.0107 \text{ cm}^2$	
$\Sigma afq = 0.01318 \text{ cm}^3$		$\Sigma afq = 0.02849 \text{ cm}^3$	
$k = 3.02 \text{ dyne cm/rad}$		$k = 3.03 \text{ dyne cm/rad}$	

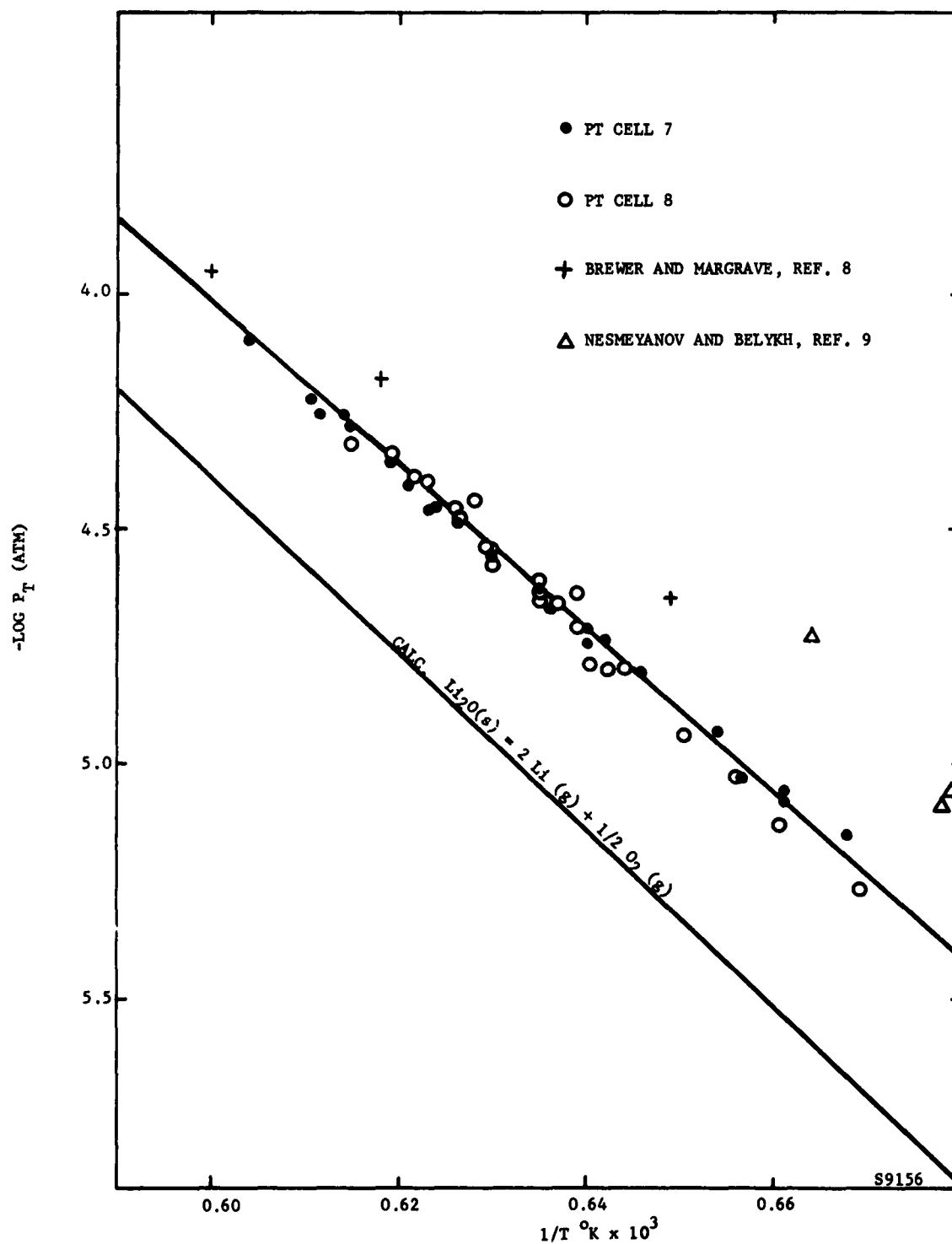


FIGURE 2. THE VAPOR PRESSURE OF LITHIUM OXIDE

vapor at Knudsen pressures. The reason for the difference between the effusion and mass spectrometric results is not apparent. If the presently accepted heat of sublimation of lithium is lowered by 4 kcal/mole, measured and calculated decomposition pressures, as well as effusion and mass spectrometric results, will be brought into agreement. Although such an error in the heat of sublimation seems unlikely, it should be checked through additional vapor pressure measurements. Because a large number of reproducible measurements were obtained, in addition to those in Table III, using a number of different samples, the torsion vapor pressure data reported here are felt to be reliable.

The results of Berkowitz, et al.¹⁰, indicate that Li_2O is the most important gaseous oxide molecule under neutral conditions. However, large uncertainties in the thermal functions of Li_2O (g) make it difficult to obtain reliable thermal properties for this substance. If the measured total pressures are corrected for the amount which is due to elemental decomposition, one calculates third-law heats of sublimation at 298°K for Li_2O (g) ranging from 97 to 101 kcal/mole, using gaseous free-energy functions from various sources.¹⁰⁻¹² A selected value of 100 kcal/mole for the heat of sublimation leads to a heat of formation of -42 kcal/mole for Li_2O (g) at 298°K. It is difficult to estimate probable errors in this value because of the aforementioned uncertainties, but limits of ± 10 kcal/mole seem not unreasonable. A more complete analysis of thermal properties can be made when reliable vibrational frequency data for Li_2O are available and the discrepancy between effusion and mass spectrometric results is cleared up.

2.4 THE VAPORIZATION OF LITHIUM METABORATE

The vapor pressure of lithium metaborate, LiBO_2 , is currently being measured by the torsion method over the range 1150 to 1300°K.

Measurements have been made with two different samples, one prepared by dehydration of Lithium Corporation of America $\text{LiBO}_2 \cdot \text{H}_2\text{O}$ and one by heating stoichiometric amounts of Li_2CO_3 and B_2O_3 . The measured vapor pressures are about three orders of magnitude higher than the pressures of either pure oxide, which would indicate formation of a stable gaseous mixed oxide molecule. A discussion of thermal properties will be withheld until the data have been completely analyzed.

2.5 THE VAPORIZATION OF BERYLLIUM FLUORIDE

a. Vaporization Under Neutral Conditions

The vapor pressure of beryllium fluoride has been measured by the torsion-effusion method over the range 810 to 945°K. Measurements were made in a resistance-heated apparatus very similar to that described in previous reports. Temperatures were measured with a chromel-alumel thermocouple which was calibrated in situ. A series of comparison measurements of the vapor pressure of potassium chloride gave excellent agreement with accepted literature values.¹³

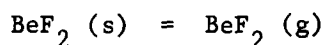
The sample of BeF_2 was obtained from Brush Beryllium Company as material of 99-percent purity; a small amount of water impurity was removed by pumping prior to the measurements. The results obtained with three graphite effusion cells of varying orifice size are presented in Table IV and are shown graphically in Figure 3. Observed pressures were independent of orifice size. Figure 3 shows the torsion data to be in good agreement with the extrapolated transpiration results of Sense and Stone¹⁴ and to be about 30-percent higher than the Knudsen effusion data of Khandamirova, et al.¹⁵

A mass spectrometric study¹⁶ has shown the saturated vapor of BeF_2 to be highly monomeric. On this basis, the heat of sublimation of

TABLE IV

THE VAPOR PRESSURE AND HEAT OF SUBLIMATION

OF BERYLLIUM FLUORIDE



Cell 12			Cell 13		
$T^\circ\text{K}$	$P_T \times 10^5, \text{ atm}$	$\Delta H_{298}, \text{ kcal/mole}$	$T^\circ\text{K}$	$P_T \times 10^5, \text{ atm}$	$\Delta H_{298}, \text{ kcal/mole}$
811.3	0.106	57.1	879.8	1.22	57.3
821.1	0.161	57.1	890.5	1.82	57.2
832.6	0.234	57.2	892.6	2.00	57.1
842.8	0.340	57.1	906.3	3.21	57.1
849.7	0.438	57.2	911.0	3.74	57.0
863.6	0.728	57.1	921.0	5.25	57.0
880.2	1.27	57.2	928.7	6.62	57.0
886.0	1.52	57.1	937.3	8.84	56.9
894.1	2.00	57.2	941.6	10.00	57.0
901.8	2.59	57.2	945.7	11.63	56.8
912.3	3.56	57.2			
920.5	4.64	57.2			

Cell 14

$T^\circ\text{K}$	$P_T \times 10^5, \text{ atm}$	$\Delta H_{298}, \text{ kcal/mole}$
840.0	0.281	57.4
853.1	0.454	57.3
871.4	0.933	57.2
886.4	1.58	57.2
896.9	2.28	57.1
903.5	2.86	57.1
911.3	3.67	57.1
921.1	4.99	57.1

Av. 57.1 ± 0.1

	$\bar{a}, \text{ cm}^2$	$\Sigma afq, \text{ cm}^3$	$k, \text{ dyne cm/rad}$
Cell 12	0.0125	0.02082	2.33
Cell 13	0.0047	0.00595	2.31
Cell 14	0.0184	0.01819	2.31

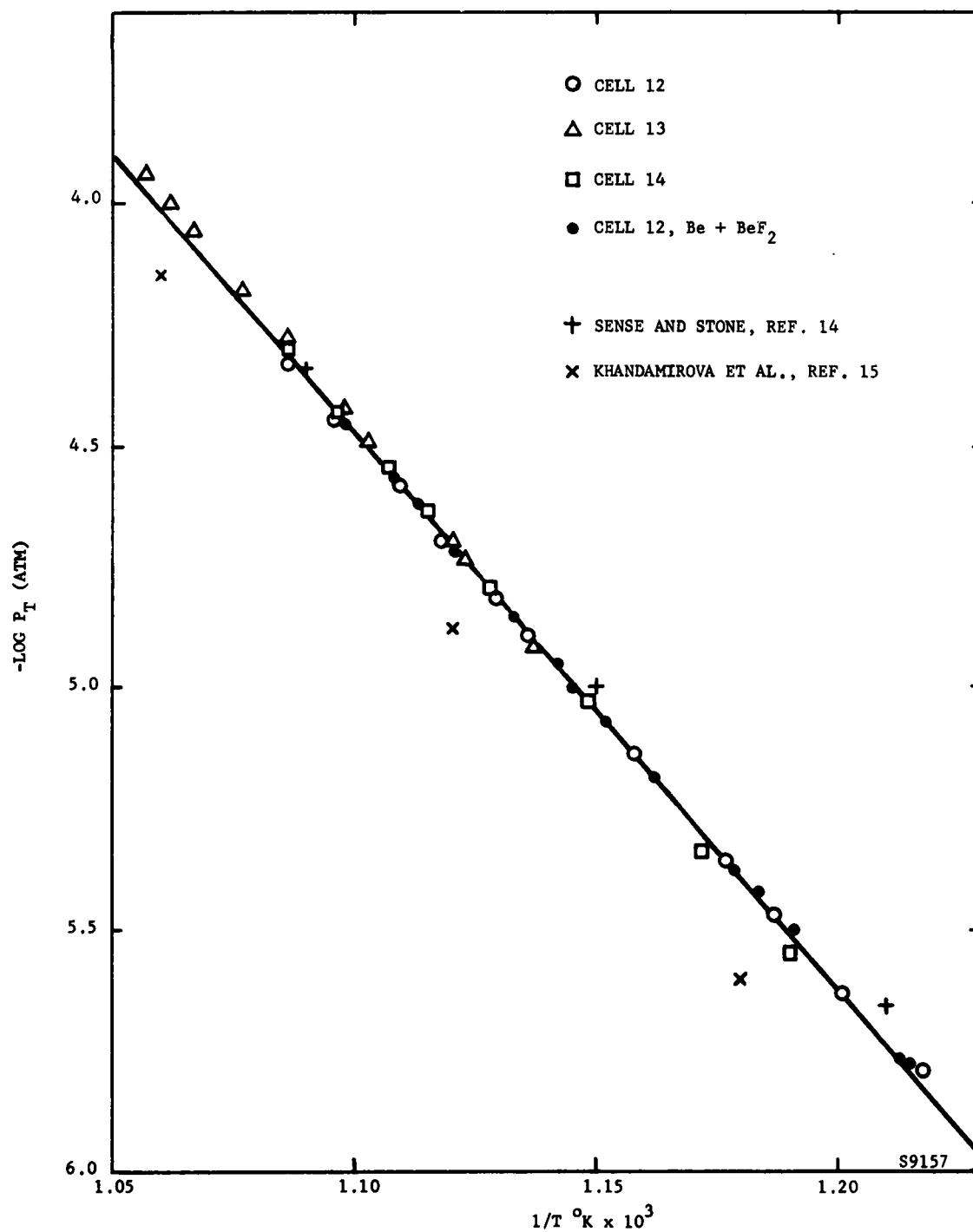


FIGURE 3. THE VAPOR PRESSURE OF BERYLLIUM FLUORIDE

BeF₂ monomer has been calculated from the vapor pressure data using free-energy functions for gaseous and condensed phases given in the JANAF tables.¹¹ The third-law heats are given in Table IV; an average ΔH_{298} of 57.1 ± 0.1 kcal/mole is obtained. Although the free-energy functions for the gas are based on reliable spectroscopic data, only estimated functions are available for condensed BeF₂. However, the estimated functions given in reference 11 appear quite reasonable when compared with well-established functions for other light-metal fluorides. A set of free-energy functions for condensed BeF₂ estimated independently at the National Bureau of Standards¹⁷ yield a third-law ΔH_{298} of 58.4 kcal/mole, about one kcal/mole higher than the values in Table IV. From the temperature dependence, a second-law ΔH at 870°K is calculated as 52.6 ± 1 kcal/mole, which reduces to 58.4 kcal/mole at 298°K, in good agreement with the third-law values. An average heat of sublimation at 298°K of 58.0 ± 2 kcal/mole is selected; the uncertainty will be reduced when more reliable free-energy functions for condensed BeF₂ become available.

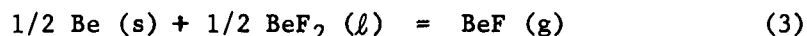
The heat of formation of crystalline BeF₂ at 298°K has been recently determined as -241.2 ± 0.8 kcal/mole by Kolesov, Popov and Skuratov.¹⁸ When this value is combined with the heat of sublimation, the heat of formation of BeF₂ (g) at 298°K is derived as -183.2 ± 2 kcal/mole.

b. Vaporization of Be-BeF₂ Mixtures

Tatevskii, Tunitskii and Novikov¹⁹ have recently estimated the dissociation energy of the BeF molecule as 8 ± 0.5 e.v. from an analysis of band spectra. This value is considerably higher than those given by Gaydon (4 ± 1 e.v.)²⁰ and by Herzberg (5.4 e.v.).²¹ These results lead to heats of formation at 298°K for BeF (g) of -88^{19} , $+5^{20}$, and -27 kcal/mole.²¹ If the results of Tatevskii, et al.,¹⁹ are correct, the vapor

pressure of a Be-BeF₂ mixture should be considerably higher than that of pure BeF₂ because of vaporization to BeF molecules; the data of Gaydon²⁰ and Herzberg²¹, however, indicate the BeF would not be important under these conditions, so that addition of elemental Be should have no effect on the vapor pressure of BeF₂.

To clarify the situation, the vapor pressure of a mixture of approximately equal volumes of beryllium powder and crystalline BeF₂ has been measured in graphite cell 12. As indicated in Figure 3, the vapor pressure of the Be-BeF₂ mixture was the same as that of pure BeF₂. Because the measurements were made at temperatures above the melting point of BeF₂, there should have been good contact between the two substances. On the basis of the above, the pressure of BeF (g) produced in the reaction



can be conservatively set at less than 20 percent of the pressure of BeF₂. A higher pressure of BeF would have been readily detected. Combining this limiting pressure of BeF with available free-energy functions¹¹, one calculates $\Delta H_{298} > 60.5$ kcal for reaction 3 and $\Delta H_f^0_{298} > -60$ kcal/mole (i.e., the true value must be less negative) for BeF (g). This would indicate that $D_0 < 6.8$ e.v. for BeF and that the interpretation of Tatevskii, et al.¹⁹, is incorrect. Additional thermochemical experiments are needed in order to fix D_0 more closely.

SECTION 3

TRANSPIRATION STUDIES
(THE ZIRCONIUM OXIDE-HYDROGEN CHLORIDE SYSTEM)

The reaction of gaseous hydrogen chloride with crystalline zirconium oxide is being studied by the transpiration method to obtain information about the thermal properties of vapor species in the Zr-O-Cl system. The equilibrium flow rate region has been determined, and these data, along with some preliminary results on the temperature dependence of the reaction, were presented in the previous report.⁷

Several determinations of the pressure dependence of the reaction have been made by studying the rate of ZrO_2 weight loss as a function of HCl pressure. These results have helped to clarify the reaction stoichiometry. Additional studies of the temperature dependence of the reaction have shown that there is a "break" in the transpiration rate curve at about 1150°K . The regions above and below this temperature have significantly different temperature dependences. A detailed study of the temperature effect has been made, and the results are presently being analyzed. A complete summary of the results, including derived thermal properties will be given in the next report.

SECTION 4

SPECIFIC HEAT MEASUREMENT

The vacuum cooling rate method for determining specific heats has been checked by measuring the specific heat of tantalum. The simplest possible experimental arrangement was used. A small, solid tantalum cylinder was suspended in a vacuum chamber by a thin tungsten wire. After the cylinder was heated initially by induction, the cooling rate was measured with a platinum, platinum-rhodium thermocouple spot-welded to the side of the cylinder.

The data were evaluated with the relation

$$C = \frac{-\sigma A \epsilon (T^4 - T_o^4)}{m \frac{dT}{dt}}, \quad (4)$$

where C is the specific heat, σ is the Stefan-Boltzman constant, A is the sample surface area, ϵ is the total hemispherical emissivity, T and T_o are the temperatures of the sample and the surroundings, m is the mass of the sample, and dT/dt is the cooling rate. The surface area was computed from the external dimensions of the sample, and the emissivity was taken from Worthing and Halliday²², no correction being made in either case for possible surface irregularities. It was assumed

that T_o , the temperature of the surroundings, was negligible compared with T , the sample temperature. This introduces an error in the value of the specific heat probably no larger than 10 percent in the worst cases -- i.e., at the lowest sample temperature.

In a series of twelve runs, in which the starting temperatures varied from 1300 to 1800°K, the cooling rate at a given temperature was found to be larger when the starting temperature was higher. This is illustrated graphically in Figure 4. Here, the individual data for three typical runs, started in the temperature range of 1725 to 1800°K, are shown in the upper curve. The lower two curves represent the data for runs started in the ranges 1500 to 1600°K (middle curve) and 1300 to 1400°K (lower curve). The variation in cooling rate may reflect a dependence of surface characteristics and, hence, emissivity on the initial temperature in a given run. For the calculation of the specific heat, results of the high-temperature runs were used, since emissivities were available in this temperature range.

In Table V these values of specific heat are compared with the recent results of Hoch and Johnston.²³ The agreement is satisfactory. Presumably, if certain refinements are made, such as polishing the sample surface and controlling the temperature of the surroundings, the method can yield useful specific-heat data.

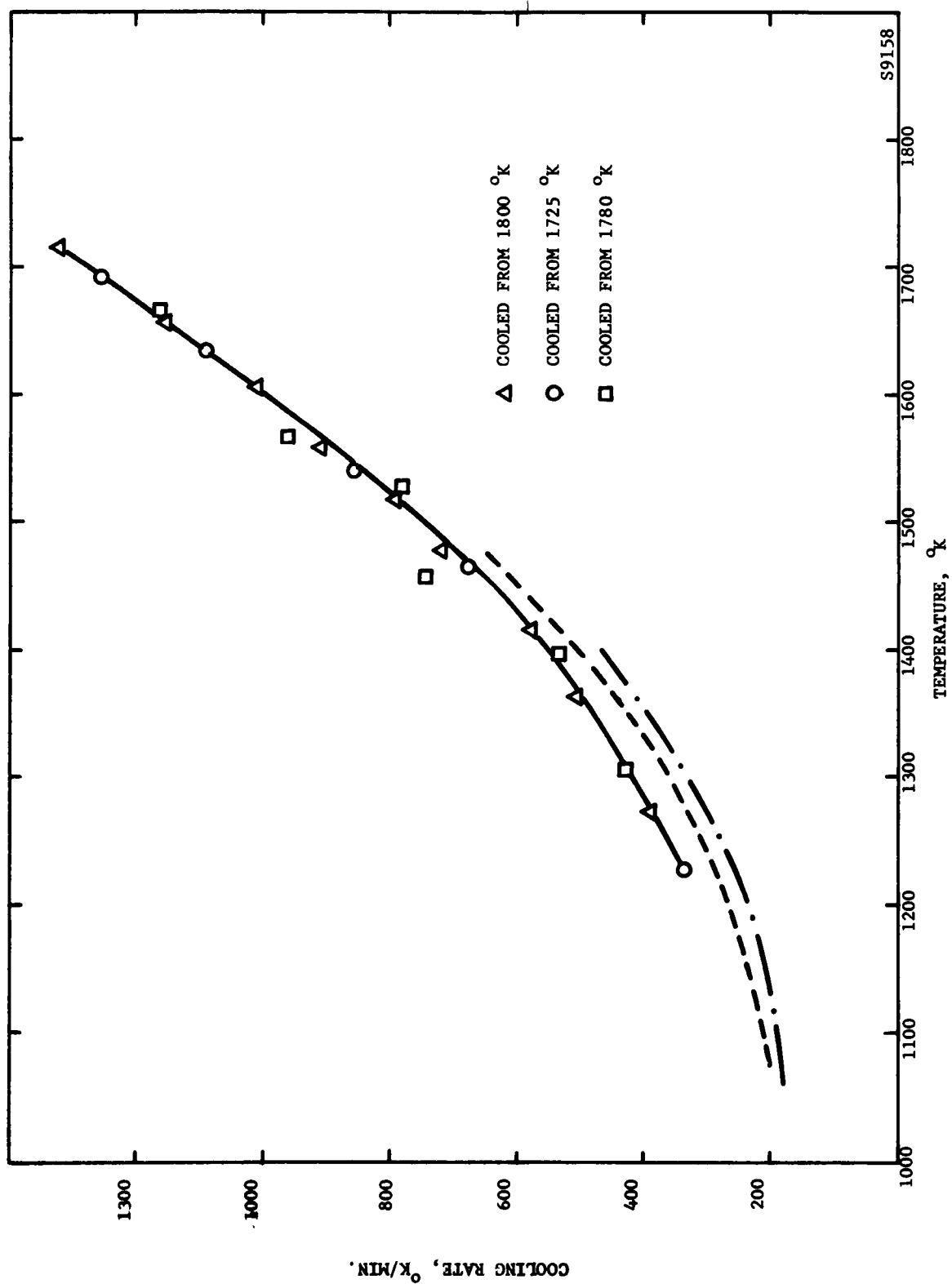


FIGURE 4. COOLING RATE OF TANTALUM SAMPLE AS A FUNCTION OF TEMPERATURE

TABLE V

THE SPECIFIC HEAT OF TANTALUM

T°K	-(dT/dt), °K/sec	C, cal/g. deg.	
		This Work	Hoch and Johnston ²³
1200	5.17	0.0320	---
1300	6.92	0.0351	0.0356
1400	9.37	0.0365	0.0357
1500	12.6	0.0372	0.0360
1600	16.9	0.0363	0.0361
1700	21.2	0.0394	0.0362

SECTION 5

MASS SPECTROMETRY

5.1 VAPOR SPECIES IN THE BORON-OXYGEN-FLUORINE SYSTEM

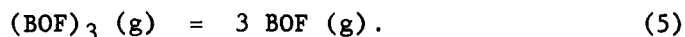
a. Experimental

During the quarter, experiments were performed with two B_2O_3 - MgF_2 samples in the mass spectrometer. The first was mixed in the mole ratio 3 B_2O_3 : 1 MgF_2 , while the second was 3 MgF_2 : 1 B_2O_3 . For experiments involving the latter a small platinum thimble containing pure B_2O_3 was placed in the Knudsen effusion cell along with the mixture.

Intensities of $^{11}BOF^+$ (m/e 46) and $(^{11}BOF)_3^+$ (m/e 138) were measured at various temperatures with the shutter slit²⁴ in both the open and closed positions. The open position is that which allows maximum transmission of the molecular beam from the Knudsen cell to the ionization chamber. In the closed position the line-of-sight path from cell to ionization chamber is blocked, but the total open area in the baffle plate which separates the Knudsen and the ion source compartments remains unchanged. The difference between ion intensity with the shutter open and with it closed (shutter-check intensity) is the intensity of ions formed by impact of electrons with molecules in the beam. Other contributions to the total intensity are due to ions formed from residual gas molecules.

b. Equilibrium Between BOF and (BOF)₃

Shutter-check intensities of BOF^+ and $(\text{BOF})_3^+$ for 17-volt ionizing electrons obtained with the 3:1 B_2O_3 - MgF_2 mixture at nine temperatures in the range 999 - 1227°K are given in Table VI. In Figure 5 the data are plotted as $\log \left[\frac{I_{\text{BOF}^+}^3 T^2}{I_{(\text{BOF})_3^+}} \right]$ versus $1/T$. The logarithmic quantity is proportional to $\log K$, where K is the equilibrium constant of the reaction¹



From the slope of the least-squares straight line drawn in Figure 5, the second-law heat for reaction 1 is derived as $\Delta H_{1113} = 126$ kcal. This value agrees within a few kilocalories with several others that were determined assuming direct proportionality between total intensities of BOF^+ and $(\text{BOF})_3^+$ for 17-volt electrons and equilibrium partial pressures of $\text{BOF} (\text{g})$ and $(\text{BOF})_3 (\text{g})$, respectively, inside the Knudsen cell. On this basis, the assumption of direct proportionality would appear to be a valid one. Experimental evidence, which will be presented in the next section, indicates the assumption to be true within limits in this case but not necessarily so for data obtained using higher ionizing electron energies.

During this and other experiments with 3:1 B_2O_3 - MgF_2 mixtures, total gas pressure inside the crucible sometimes underwent significant, though slow, fluctuations with time. Equilibrium could be maintained, but since BOF^+ and $(\text{BOF})_3^+$ intensities could not be measured simultaneously, a certain amount of error was introduced into determinations of relative intensities. A 3:1 $\text{MgF}_2 + \text{B}_2\text{O}_3$ mixture, being stoichiometric for production of $\text{BF}_3 + \text{MgO}$, might produce BF_3 gas at a steadier rate. On the other hand, with such a mixture the B_2O_3 surface area available to BF_3 might not be sufficient to satisfy Knudsen requirements. A larger B_2O_3 surface area can be provided, however, by placing a separate container filled with B_2O_3 inside the effusion cell.

TABLE VI
 TEMPERATURE STUDY OF BOF^+ AND $(\text{BOF})_3^+$ INTENSITIES
 FOR A 3:1 B_2O_3 - MgF_2 MIXTURE*
 IONIZING VOLTAGE = 17 VOLTS

T °K	Shutter-check Intensity**		Log $\frac{I_{\text{BOF}^+}^3 T^2}{I_{(\text{BOF})_3^+}}$
	I_{BOF^+}	$I_{(\text{BOF})_3^+}$	
	m/e 46	m/e 138	
999	0.2	0.7	4.08
1044	1.0	0.7	6.19
1087	3.3	2.6	7.21
1123	9.1	7.7	8.09
1108	4.0	3.6	7.34
1160	16.3	10.2	8.76
1198	34.0	25.6	9.34
1179	18.0	9.6	8.93
1227	51.3	32.7	9.79

* Effusion cell contained a portion of a 3:1 mole ratio mixture of B_2O_3 and MgF_2 , respectively.

** Difference between intensities (arbitrary units) with shutter open and shutter closed.

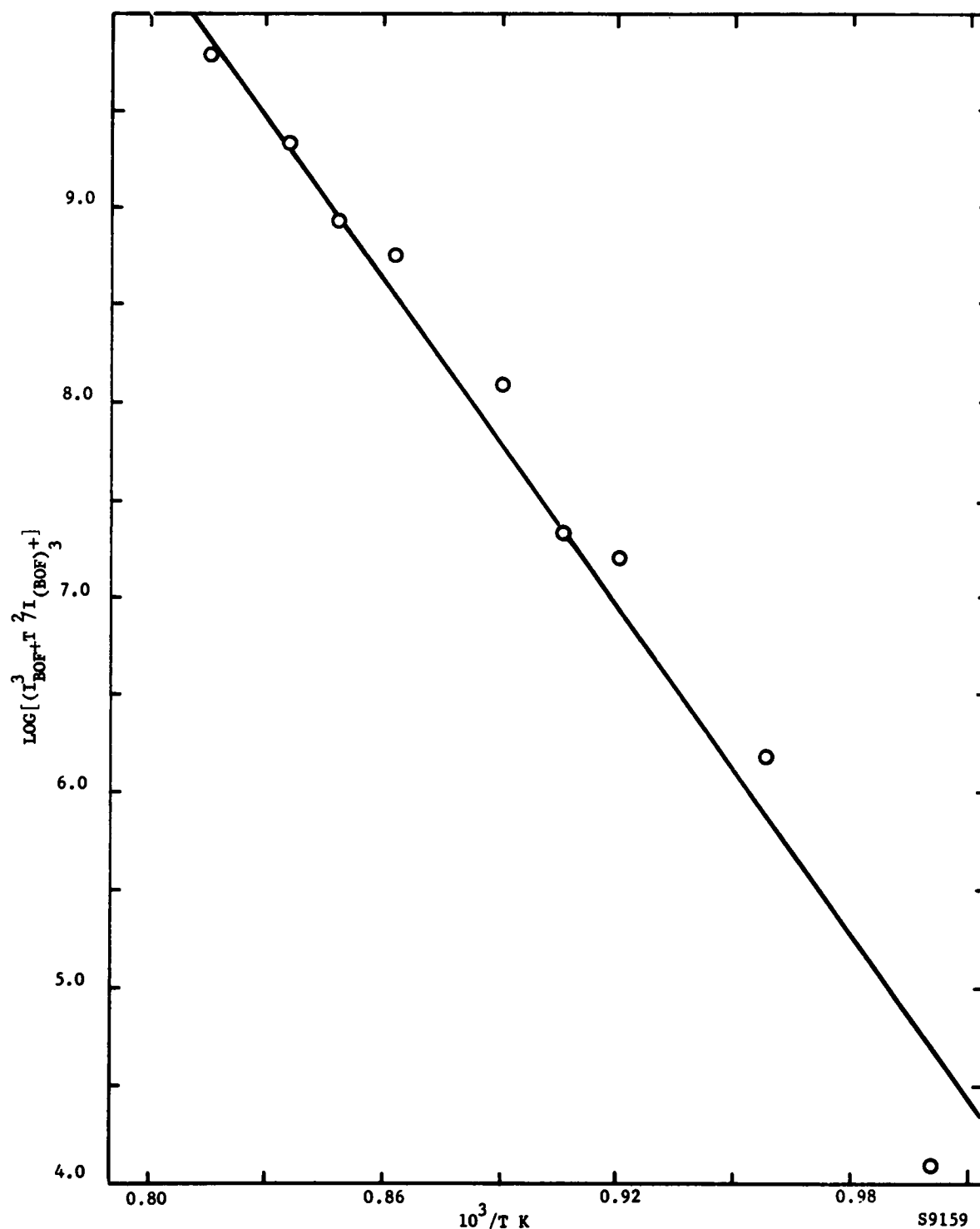


FIGURE 5. TEMPERATURE STUDY OF THE BOF MONOMER-TRIMER EQUILIBRIUM FOR 3:1 B_2O_3 - MgF_2 MIXTURE

A small platinum thimble supported by a tungsten tripod was filled with pure B_2O_3 and placed in a tungsten effusion cell along with a portion of a 3:1 mole ratio $MgF_2 - B_2O_3$ mixture. BOF^+ and $(BOF)_3^+$ shutter-check intensities measured over the temperature range 979 - 1229 °K with an ionizing electron energy of 17 volts are given in Table VII. Measurements were made randomly, not in the order of listing. After thermal equilibration, ion intensities at each temperature became quite steady. In Figure 6, $\log I_{BOF^+}^3 T^2 / I_{(BOF)_3^+}$ is plotted against I/T , and the straight line obtained by least-squares analysis is drawn. Although the slope of this line is very nearly equal to that of Figure 5, the points of Figure 6 have a smaller root-mean-square deviation and are therefore preferred for use in evaluating the second-law heat. The heat of reaction 5 derived from the slope of Figure 6 is $\Delta H_{1125} = 131$ kcal. From estimated thermal functions, $\Delta(H_{298}^{1125})$ for the reaction is -3.1 kcal. Thus $\Delta H_{298} = 134$ kcal. Combining the latter with $\Delta H_{298}^0 [(BOF)_3(g)] = -566$ kcal/mole²⁵ gives $\Delta H_{298}^0 [BOF(g)] = -144$ kcal/mole, with an estimated experimental uncertainty of ± 3 kcal/mole.

Although the total gas pressure inside the crucible, $P [BF_3(g)] + P [BOF(g)] + P [(BOF)_3(g)]$, was not the same for all measurements of Table VII, equilibrium was maintained throughout. For a given temperature, the $BOF^+ / (BOF)_3^+$ intensity ratio was a function of $BF_3(g)$ pressure (which could be monitored with BF_3^+ or BF_2^+). Absolute intensities, however, were always of such magnitudes as to maintain a constant value for $\log [I_{BOF^+}^3 T^2 / I_{(BOF)_3^+}]$.

c. Shutter Effects

As stated earlier, previous determinations of ΔH for reaction 5 based on total ion intensities for 17-volt electrons agree approximately with current values derived from shutter-check intensities. In obtaining the data of Table VII, both total and shutter-check intensities of BOF^+ and

TABLE VII
TEMPERATURE STUDY OF BOF^+ AND $(\text{BOF})_3^+$
INTENSITIES FOR A 3:1 $\text{MgF}_2\text{-B}_2\text{O}_3$ MIXTURE*

IONIZING VOLTAGE = 17 VOLTS

T °K	SHUTTER-CHECK INTENSITY**		Log	$\frac{I_{\text{BOF}^+}^3 T^2}{I_{(\text{BOF})_3^+}}$	$\frac{I_{\text{BOF}_3^+}}{I_{(\text{BOF})_3^+}}$	Shutter-check $\frac{I_{(\text{BOF})_3^+}}{\text{Total } I_{(\text{BOF})_3^+}}$
	I_{BOF^+}	$I_{(\text{BOF})_3^+}$				
	m/e 46	m/e 138				
979	< 2.0	53			< 0.04	0.17
1021	4.8	29	6.60		0.17	0.16
1057	8.0	25	7.36		0.32	0.19
1097	23.3	68	8.35		0.34	0.19
1136	38	43	9.22		0.88	0.16
1152	30	15	9.38		2.00	0.22
1155	57	45	9.74		1.27	0.16
1174	72	58	9.95		1.24	0.18
1184	79	33	10.32		2.39	0.15
1202	99	30	10.67		3.30	0.15
1229	120	16	11.21		7.50	0.11

* Effusion cell contained a portion of a 3:1 mole ratio mixture of MgF_2 and B_2O_3 , respectively, together with a small platinum thimble filled with pure B_2O_3 .

** Difference between intensities (arbitrary units) with shutter open and shutter closed.

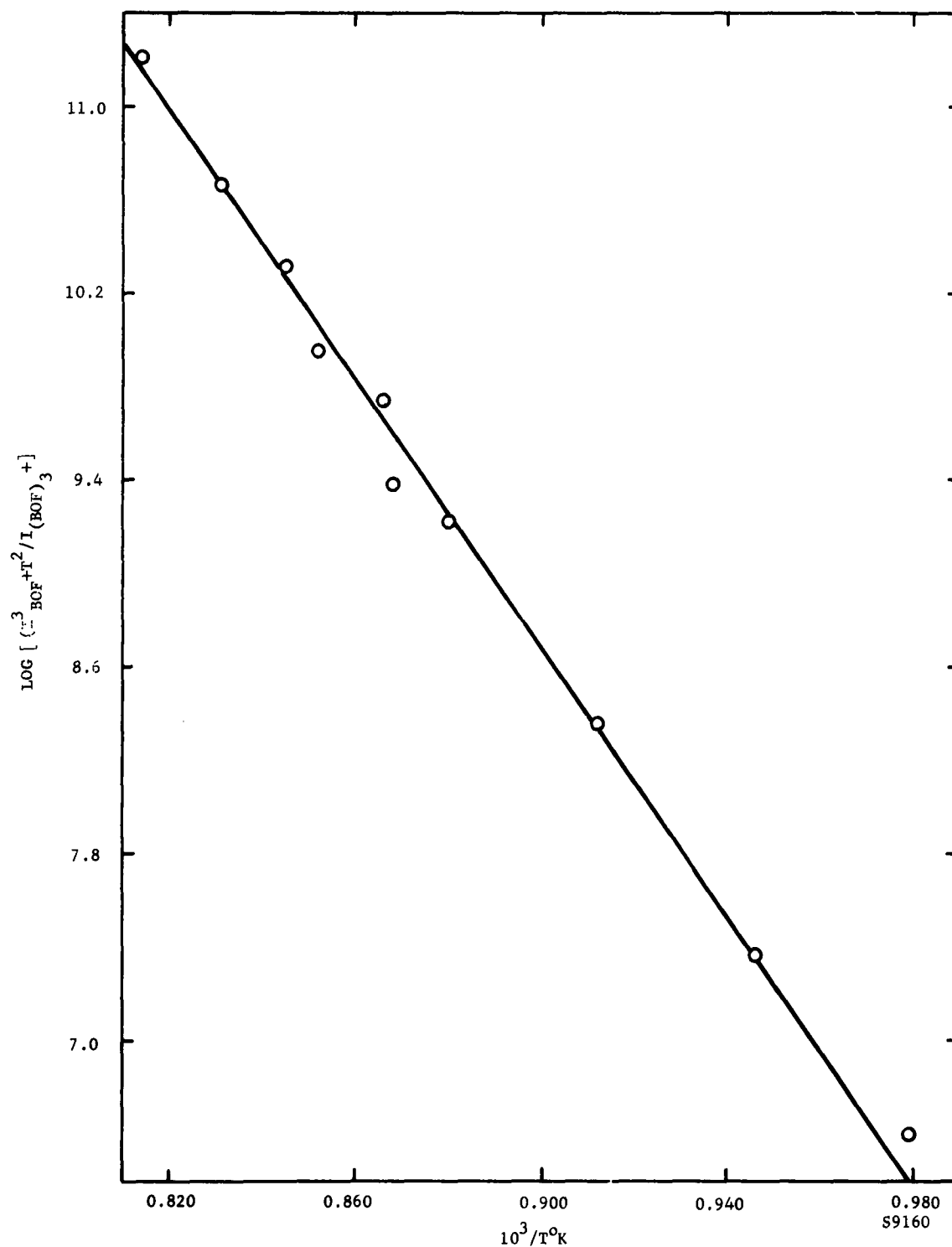


FIGURE 6. TEMPERATURE STUDY OF THE BOF MONOMER-TRIMER EQUILIBRIUM FOR 3:1 $\text{MgF}_2\text{-B}_2\text{O}_3$ MIXTURE

$(\text{BOF})_3^+$ were measured. Under the conditions of the experiment BOF^+ gave a 100-percent shutter check--that is, the entire BOF^+ ion signal (m/e 46 and 46) was suppressed by closing the shutter. Thus, the BOF^+ intensities given are also total intensities. With $(\text{BOF})_3^+$ only a fractional reduction of intensity was observed when the shutter was closed. But the magnitude of the reduction, as can be seen in the last column of Table VII, did not vary greatly with temperature. At nine of the eleven temperatures the intensity reduction was 17 ± 2 percent. Thus, shutter-check intensities of both BOF^+ and $(\text{BOF})_3^+$ are roughly proportional to total intensities, and the most serious consequence of substituting one for the other in a second-law plot of the data is a change in the intercept of the straight line. The slope does not change greatly, and, hence, neither does the value of ΔH derived from it.

It should be emphasized strongly that this result is by no means of general significance, for even in the present case it is only observed with ionizing voltages in the vicinity of 17 volts. Beginning at slightly higher voltages the m/e 45 mass position is partially occupied by $^{13}\text{CO}_2^+$ and m/e 46 by $^{10}\text{BFOH}^+$ and perhaps certain fragment ions from hydrocarbon molecules. These contributions are not proportional to the equilibrium partial pressure of BOF inside the crucible. Therefore, total intensities obtained with higher ionizing voltages cannot be used for second-law determination of ΔH for reaction 5.

Relative heights of the m/e 135-138 peaks are not affected by the action of the shutter; only the absolute intensities change. Obviously, $(\text{BOF})_3$ (g) does not condense completely inside the mass spectrometer but behaves instead somewhat as a permanent gas. When $(\text{BOF})_3$ (g) is being produced inside the crucible, a steady-state pressure of the vapor exists in each of the compartments of the instrument, and that pressure depends upon the geometry of the compartment, the rate at which the vapor leaks in, and the rate at which it is pumped out. When the shutter is open, not

only is $(\text{BOF})_3$ (g) streaming from the crucible into the ion-source compartment, but it also leaks from the body of the Knudsen compartment to the source by way of the shutter slit. The observed $(\text{BOF})_3^+$ intensity is due to ions formed by ionization of $(\text{BOF})_3$ molecules both from the background vapor and from the molecular beam issuing from the crucible. If the Knudsen compartment is completely closed off from the source, the $(\text{BOF})_3^+$ intensity drops suddenly by an amount corresponding to the fractional contribution of the molecular beam to the total rate of ion formation. Then a more gradual rate of decrease begins as the background $(\text{BOF})_3$ level starts to drop and continues until the evacuation limit of the pumping system is reached. One would experience difficulty in attempting to determine accurately the contribution of the molecular beam from such an experiment. Ideally, one should suppress only a single contribution in a shutter experiment. For $(\text{BOF})_3$ (g) this can be done approximately by positioning the shutter slit in such a way that the line-of-sight path from Knudsen cell to ionization chamber is blocked, but the total open area between Knudsen and source compartments is unchanged. Passage directly from crucible to ionization chamber is no longer possible; but leakage from Knudsen compartment to source by way of the shutter slit continues, and background pressure is maintained. Ion intensities given in Tables VI and VII were obtained by this method.

d. Mass Spectral Considerations

Concrete evidence for the absence of appreciable fragmentation of $(\text{BOF})_3$ (g) to form BOF^+ ions at 17-volt ionizing voltage is given in Table VIII. The $I_{\text{BOF}^+}/I_{(\text{BOF})_3^+}$ shutter-check intensity ratio for each temperature, is given in the fifth column. At the lowest temperature, 979°K, the ratio was less than 0.04, while at 1229°K it was 7.50, more than two orders of magnitude larger. Since the electron impact cracking pattern of $(\text{BOF})_3$ (g) is not likely to change drastically for a temperature change of only 250 degrees²⁶, an upper limit for the relative

TABLE VIII
 MASS SPECTRAL DATA FOR B-O-F SYSTEM*
 $T = 1229^{\circ}\text{K}$

m/e	Species	I V** = 70 Volts		I V = 17 Volts	
		Shutter Open	Shutter Closed	Shutter Open	Shutter Closed
44	$^{12}\text{CO}_2^+$	134	135	2.9	3.0
45	Total	35	24	2.9	--
	$^{13}\text{CO}_2^+$	1.5	1.5	--	--
	$^{10}\text{BOF}^+$	<u>33.5</u>	<u>22.5</u>	<u>2.9</u>	--
46	Total	220	164	10.9	0.3
	$^{11}\text{BOF}^+$	<u>144</u>	<u>92</u>	<u>10.6</u>	--
	$^{10}\text{BFOH}^+$	76	72	0.3	0.3
47	$^{11}\text{BFOH}^+$	328	310	1.4	1.5
	$^{10}\text{BOF}^+ / ^{11}\text{BOF}^+$	0.23	0.24	0.27	
138	$(^{11}\text{BOF})_3^+$	162	143	5.5	4.9

* $\text{MgF}_2 - \text{B}_2\text{O}_3$ sample same as that described in Table VII.

** I V = ionizing voltage.

intensity of BOF^+ produced by fragmentation at all the temperatures of Table II is 0.04. Thus, at the lowest temperature used for Figure 2, 1021°K , the BOF^+ Contribution from fragmentation was less than 23 percent and at 1229°K less than 0.5 percent.

At 70 volts ionizing voltage there appears to be extensive BOF^+ production by fragmentation of $(\text{BOF})_3$ (g). The mass 45 and 46 peaks are not completely suppressed at 70 volts by closing the shutter, although intensity ratios of residuals at these masses, after correction for $^{13}\text{CO}_2^+$ and $^{10}\text{BFOH}^+$ contributions, are equivalent to the $^{10}\text{B}/^{11}\text{B}$ natural abundance ratio. Table VI gives intensities of the m/e 44, 45, 46, and 47 peaks for 70-volt and for 17-volt electrons both with the shutter open and with the shutter closed, obtained using the sample described at the bottom of Table VII. Temperature was 1229°K . The $^{10}\text{BFOH}^+$ contribution to the peak at m/e 46 was determined by multiplying the m/e 47 intensity, assumed to be caused only by $^{11}\text{BFOH}^+$, by the $^{10}\text{B}/^{11}\text{B}$ natural abundance ratio 0.232. The ^{11}BOF intensity was obtained by subtracting $^{10}\text{BFOH}^+$ from total m/e 46. Similarly, the $^{13}\text{CO}_2^+$ contribution to m/e 45 was obtained from the $^{12}\text{CO}_2^+$ intensity and the $^{13}\text{C}/^{12}\text{C}$ natural abundance ratio 0.0112. The $^{10}\text{BOF}^+$ intensity was then determined by subtracting $^{13}\text{CO}_2$ from total m/e 45. Ratios of $^{10}\text{BOF}^+ / ^{11}\text{BOF}^+$ obtained in this way are given at the bottom of Table VIII and are in agreement with the $^{10}\text{B}/^{11}\text{B}$ natural abundance ratio, indicating the analysis to be correct.

Residual BOF^+ observed for 70-volt electrons with the shutter closed cannot be caused by ionization of BOF (g), since the data for 17-volt electrons indicate 100-percent suppression of ion current produced by this species when the shutter is closed. Consequently, it must be caused by fragmentation of background $(\text{BOF})_3$ (g). If this is so, the shutter-check intensity of BOF^+ contains a fragmentation contribution that is derived from $(\text{BOF})_3$ (g) present in the molecular beam.

5.2 THE BERYLLIUM-OXYGEN AND BERYLLIUM-OXYGEN-HYDROGEN SYSTEMS

The mass spectrometer is being used in another Aeronutronic program [Contract AF 04(611)-7442] for studying vapor species in the Be-O and Be-O-H systems. A summary of recent results is presented below.

Mass spectrometric studies of the BeO-H₂O system were carried out at 1938 °K. Under the conditions of the experiments no detectable amounts of gaseous hydroxide species were present. However, a lower limit of -181 kcal/mole for the heat of formation of Be(OH)₂ (g) at 298 °K was derived from mass spectral data.

A mixture of beryllium metal and beryllium oxide in the mass spectrometer gave evidence for the presence of Be (g) in the equilibrium vapor at temperatures up to 1800 °K. No evidence for Be₂ (g) and Be₂O (g) was obtained, contrary to reports of others²⁷.

Mass spectra for the Be - BeO mixture in the presence of water vapor contained no measurable intensities of BeOH⁺ at 1800 °K. A lower limit of -21 kcal/mole was derived for the heat of formation of BeOH (g) at 298 °K.

SECTION 6

SUMMARY OF THERMODYNAMIC DATA

An up-to-date summary of thermodynamic data obtained as part of this experimental program is given in Table IX. The data are revised as necessary when newer and more reliable auxiliary data used in their derivation appear. $\Delta H_{\text{sub}, 298}$ and $\Delta H_f^0_{298}$ represent the derived heats of sublimation and heats of formation at 298°K.

TABLE IX
SUMMARY OF EXPERIMENTALLY DETERMINED
THERMAL DATA
Contracts NOrd 17980 and NOw 61-0905

Species	$\Delta H_{\text{sub}, 298}$ kcal/mole	$\Delta H_f^{\circ}_{298}$ kcal/mole	References
LiF(g)	65.3 ± 0.3	-79.8 ± 1.3	7, 28, 29
Li ₂ F ₂ (g)	69.3 ± 1	-220.9 ± 1.6	7, 28, 29
LiCl(g)	49.9 ± 0.3	-47.8 ± 2	7, 28, 29
Li ₂ Cl ₂ (g)	50.6 ± 1	-144.8 ± 2.3	7, 28, 29
BOF(g)		-144 ± 3	1, 7, 24
(BOF) ₃ (g)		-566.2 ± 2.7	25
MgF ₂ (g)	85.9 ± 1	-178.1 ± 4	25
BN(s)		-59.8 ± 0.7	25
ZrF ₄ (g)	55.8 ± 2	-401.1 ± 2	24, 25
AlF ₃ (g)	71.0 ± 0.5	-285.3 ± 2	1, 24
LiAlF ₄ (g)	65 ± 3	-447 ± 7	1, 24
AlN(s)		-76.1 ± 2.1	1, 7
B ₂ O ₃ (g)	$99.0 \pm 3^*$	-202.0 ± 3	
Li ₂ O(g)	100 ± 10	-42 ± 10	
Mg Cl ₂	63.3 ± 2	-243.5 ± 2	7
BeF ₂ (g)	58.0 ± 2	-183.2 ± 2	
BeF(g)		> -60	

* $\Delta H_{\text{vap}, 298}$

SECTION 7

FUTURE PROGRAM

The vaporization of lithium aluminate and beryllium chloride will be studied by the torsion-effusion method.

Following completion of studies on the $\text{ZrO}_2\text{-HCl}$ system, transpiration measurements on the $\text{B}_2\text{O}_3\text{-HCl}$ system will be initiated.

Ionization efficiency curves and shutter profiles will be obtained for BOF^+ and $(\text{BOF})_3^+$ ions in order to complete the interpretation of the mass spectral data on the B-O-F system. Mass spectrometric studies of the vaporization of magnesium chloride, now in progress, will be continued.

The applicability of the vacuum cooling rate method to measurement of the specific heats of powdered samples will be studied in more detail. Previous results indicate that heat transfer within the sample must be improved.

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